

PRELIMINARY STUDIES ON THE EXHAUSTION OF LOW-GRADE MASSECUITES

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Abstract

Factorially designed experiments were carried out in a pilot crystalliser to investigate C-masseccuite total solids and true purity, retention, cooling and stirring rates, to optimise exhaustion. Preliminary results show masseccuite non-sucrose/water ratio to be a statistically significant factor, having a direct relationship with exhaustion. This ratio may be increased by increasing total solids and lowering purity of C-masseccuites, total solids having a far more pronounced effect. Of the other factors, only retention time was shown to be statistically significant. Curve fitting techniques are also used to model crystalliser performance. This quantifies the effects of stirring which is not usually possible by other methods. This technique also allows comparisons to be made by separating the effects of masseccuite quality and crystalliser performance.

Introduction

Of the many factors affecting the exhaustion of low purity masseccuites, some, like the type of impurity present, cannot be controlled while others, like masseccuite brix or purity may readily be changed by factory personnel. Investigation of those controllable factors would therefore yield results which would be applicable on the factory scale relatively quickly.

Using this approach, C-masseccuite brix, C-masseccuite purity, stirring rate, cooling rate and retention time in the crystallisers were selected for investigation.

These particular factors are well documented in the literature, mostly on an individual rather than interactive basis. Work done in Australia^{1,2,3} shows that crystallisation continues even at low purities and that the only real controlling factor is the high viscosity of the material at low purities.

West¹⁸ states that the purity of C-masseccuite appears to have no effect on either mother liquor purity at strike or on final purity after cooling, which was evident both from laboratory and factory work. In the discussion of this paper however, the validity of this statement is queried by Birkett. Using pilot plant equipment, West¹⁸ stresses the importance of retention in the crystallisers and shows that the highest possible masseccuite brixes are to be aimed for.

In South Africa, Graham⁴ also shows the importance of high masseccuite brixes. He discusses the effect of purity on the amount of masseccuite to be handled but does not mention its effect on exhaustion as such.

Cooling rates have been studied by Relf¹⁴ who arrives at the conclusion that, irrespective of the rate of cooling in his pilot-crystalliser the exhaustion achieved was the same after about 30 hours.

Jullienne⁷ using factory data stresses the importance of C-masseccuite purity on exhaustion. Using an approach involving high A-masseccuite exhaustion and low C-masseccuite purity he achieved excellent results.

Morgan¹¹ using multi-linear regressions showed a statistically significant direct relationship between final molasses purity and C-masseccuite purity. The data could not be used for the investigation of masseccuite brix but, using the impurity/water ratio concept, Morgan¹² shows that high masseccuite brixes are to be aimed for.

Smythe¹⁷ in his excellent review on crystal growth, covers the effect of stirring on crystallisation, on the laboratory scale. In pure sucrose solutions,¹⁵ the crystallisation rate at constant

supersaturation tends asymptotically to a limit (at approximately double the rate without stirring) as stirring increases. Quantitative data for factory scale operation is rather scarce.

Experimental

The experimental approach used for the investigation of the selected factors was given careful consideration. The operational flexibility required demanded pilot plant scale, which however is often not representative because of its relatively small size while also presenting scale up problems. The following requirements were thus drawn out:-

- The plant would be of a capacity that would allow relatively large quantities of masseccuite to be treated. This also allows samples to be taken throughout the treatment without reducing the level of masseccuite too much.
- It would provide stirring and cooling (or reheating) facilities which would include and bracket as widely as possible, usual factory levels.

Reference to Perry¹³ revealed that the above requirements would be met by Kneader - Mixers or Z blade mixers. One such mixer was therefore obtained with the following specifications:

Working capacity	80 litre
Surface area jacketed for water flow	35%
Surface area/volume ratio	15m ² /m ³
Stirring variable	3 to 6 rpm

At this stage it was thought that the stirring levels of the mixer, even at the lower rpm, would be very much higher than those used in industrial crystallisers. These high levels could have two serious adverse effects, namely air entrainment into the masseccuite resulting in viscosity increases, and heat generation which would prevent or reduce cooling. Both these were in fact found to occur at 3 rpm and above. It was therefore planned to reduce rotational speeds to the range ¼ to 2 rpm. This eliminated the air entrainment problem but there was still some evidence of heat generation with high total solids masseccuites at the lower temperatures, that is at higher viscosities. A further reduction to rotational speeds around ¼ rpm will be available for future tests.

The complete plant is shown schematically in Figure 1. Figure 2 shows the mixer itself.

The plant is situated directly above a crystalliser of the Darnall mill, masseccuite being fed in through a flexible plastic hose. This hose is connected through valves, directly to the saucers of two of the mill C-pans, which allows masseccuites to be obtained at any stage through a boiling. This arrangement has increased experimental flexibility tremendously.

Although the experiment concerned only the selected factors, it was realised that changes in both type and quantity of impurities in the masseccuites would have a very pronounced effect on exhaustion. Since these changes cannot be controlled, it was decided to adopt an experimental approach which would give an indication of, and possibly help reducing, the effects of these changes.

The approach adopted involved factorially designed experiments and has been described in detail elsewhere.⁹ This approach shows interactive effects between the factors, if these effects are present, and therefore allows all factors under study to be optimised as a group rather than individually. Secondly it requires measurement of the experimental error which includes the effects of changes in masseccuite quality.

The procedure adopted for the runs consisted of setting levels for the factors and planning the necessary combinations. Replicate runs were then included as required.

- (b) Investigation of stirring rates, in isolation, through two, non-factorial series.
- (c) Closer study of massecuite total solids and purity, in a further factorial series.
- (d) A relatively complex, five factor factorial. The results and experience gained from the previous series were used to make this series as meaningful as possible.
- (e) Investigation of a number of B-massecuites, through a non-factorial series.

In total about 100 massecuites were treated in the pilot mixer, over a period of two seasons.

In all cases, trends established in one series of experiments were confirmed by the other series. Results presented here are therefore grouped together and represent the overall findings.

The overall range and levels of the factors investigated are shown in Table 1 and Figure 3.

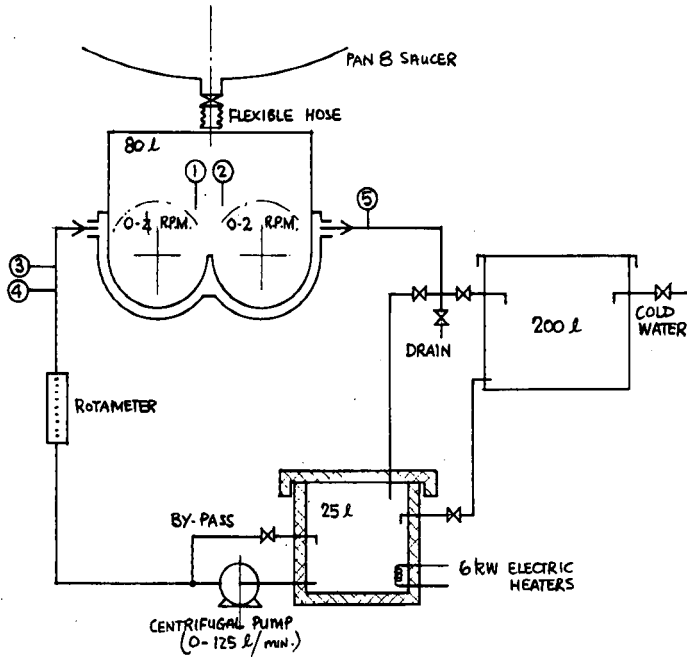


Figure 1: Schematic diagram of pilot plant.

The following data were then collected for statistical analysis:- massecuite brix, total solids (vacuum oven), and true purity, true purity and target purity difference on Nutsch molasses at various time intervals during the retention.

The analytical methods used are described in the Hulett's Laboratory Operations Manual. ¹⁹ Cooling rates (recorded by a multipoint temperature recorder), stirring rates (in rpm) and retention time (in hours) were also available.

Table 1
Range and levels of factors

Factor	Range	Levels		Remarks
		Av. high	Av. low	
Massecuite total solids	90-94	93,3	91,0	Brix: 93-98
Massecuite true purity	50-68	60,6	55,0	Apparent purity 46-62
Retention (hr)	4-15	15	4	Effect of retention was obtained through samples during test.
Stirring (rpm)	¼-6	2	¼	Intermittent stirring also used
Cooling	±60- ±40°C	Fast	Slow	Shown in Figure 3

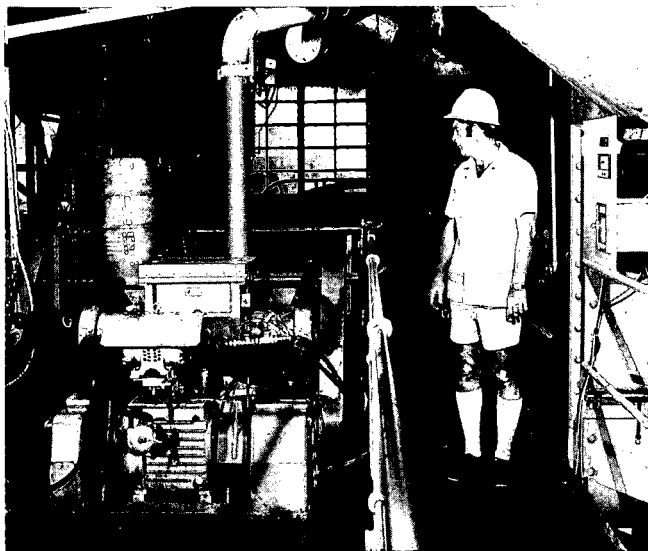


Figure 2: Pilot crystalliser.

The data were then analysed by computer using final nutsch molasses true purities and target purity differences as measures of exhaustion.

All the results reported here are based on true purities. Target purity difference usually yielded similar, if not identical, results.

The experimental approach was as follows:-
(a) A relatively short term, factorially planned screening test.

The findings of this investigation obviously apply only over the ranges shown.

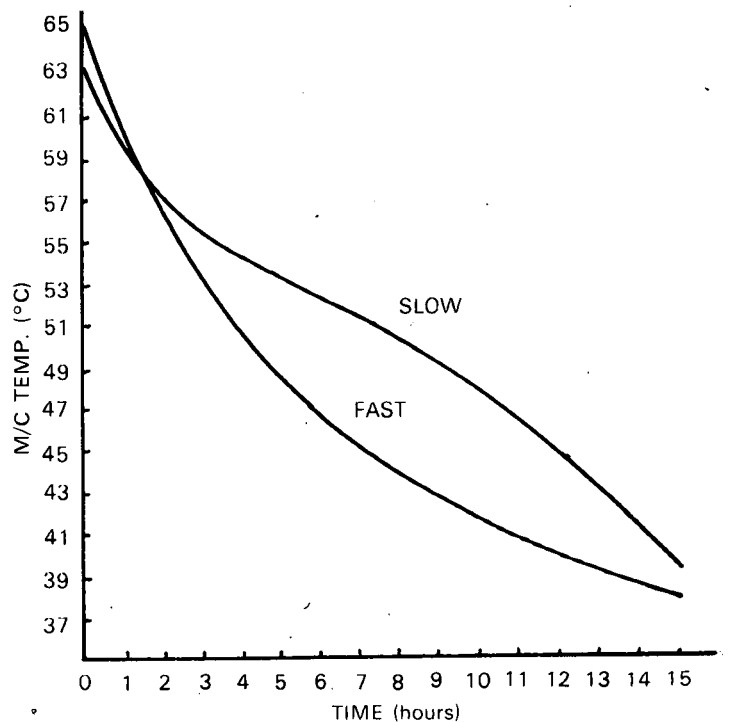


Figure 3: Range and level of factors.

Results and Discussion

Evaluation of the factorial series

1. *Massecuite total solids and true purity* -

Massecuite total solids was shown statistically to be the most important factor. The higher the massecuite total solids (or brix) the lower the final nutsch molasses true purity.

Massecuite purity on the other hand was shown to have no statistically significant effect.

The concept of non-sucrose/water ratio is shown to affect exhaustion, in the literature,^{6, 10, 12} Its effect was therefore assessed, the results being shown in Table 2.

The data used for these regressions comes only from the factorial series. This eliminates any effects due to factors not considered here. It is evident that the correlation coefficient is improved when non-sucrose/water is used.

The non-sucrose/water ratio is thus better than total solids as an indication of massecuite exhaustability, the higher the ratio, the better the exhaustion.

Massecuite non-sucrose/water ratio is given by:

$$\frac{\text{total solids \% massecuite} - \text{sucrose \% massecuite}}{100 - \text{total solids \% massecuite}}$$

and is therefore dependent on both massecuite total solids and purity.

These two parameters must thus be chosen so as to obtain the highest possible non-sucrose/water ratio, without however exceeding the limit imposed by mechanical considerations.

Regressing massecuities non-sucrose/water ratios against massecuite total solids and true purities for the massecuities involved in all the series, yields the following equation:

NS
M/c $\frac{\text{NS}}{\text{H}_2\text{O}}$ = -53,0 + 0,71 M/c total solids - 0,12 M/c true purity

Equation (3)

Equation 3 shows that a 1-unit change in total solids is equivalent to a 6-unit change in purity the effects being in opposite directions. Non-sucrose/water ratio is therefore much more influenced by total solids than it is by purity.

This equation also gives a reason for the non-significance of massecuite purity. Table 3 shows the derived relationships between molasses purity, and massecuite total solids, purity and non-sucrose / water ratio. Thus, using massecuite total solids of 93 an 90 and a constant massecuite true purity of say 55 in Equation 3, yields corresponding non-sucrose/water ratios of 6,4 and 4,3. Using these values of non-sucrose/water ratios in Equation 2 results in final molasses true purities of 35,9 and 38,3, that is a change of 2,4 units. A similar procedure using massecuite true purities of 61 and 55, results in a change of only 0,8 units in final molasses true purity.

Since the experimental error was found to be 1 unit of nutsch molasses true purity, the effect of massecuite purity would not be found significant in the factorial series.

Finally, non-sucrose/water ratio is more significant than total solids because it includes the relatively smaller effect of purity with that of total solids.

2. *Retention* -

Retention was shown to be the second and only other statistically significant factor, the longer the retention, the better the exhaustion.

Under specific conditions, particularly cooling and stirring rates, a fairly good fit, shown in Fig. 4, was obtained for the following relation:

$$\text{Nutsch molasses true purity} = a + b.e^{-ct} \quad \text{Equation (4)}$$

where a, b and c are constants, and t the retention time in hours. Equation 4 shows that, as time tends to infinity, molasses purity tends to a.

Under those specific conditions, the equations for all B and C- massecuities were:-

For B-massecuities: Molasses true purity = 38,3 + 9,2.e^{-0.20t}

For C-massecuities: Molasses true purity = 36,7 + 7,4.e^{-0.18t}

Table 2:

True purities of final nutsch molasses (TP) regressed against massecuite total solids, true purity and non-sucrose/water ratio.

Nutsch Molasses True Purity (TP) V/S:	Equation:	Corr. Coeff.	Significant	n
Massecuite total solids	1. TP = 104,3 - 0,7 Total Solids M/c	-0,46	>0,1%	53
Massecuite true purity	-	+0,15	Not. Sig.	53
Massecuite non-sucrose/wat ratio	2. TP = 43,6 - 1,2 $\frac{\text{NS}}{\text{H}_2\text{O}}$ M/c	-0,57	>0,1%	53

Table 3:

Effects of changes in massecuite true purity and total solids on nutsch molasses true purity.

Factor	Average difference between high and low levels in any one series	Equation	NS $\frac{\text{NS}}{\text{H}_2\text{O}}$ units equivalent	Equation	expected change in final molasses true purity
Massecuite total solids	3 units	Eq. No. 3	2 units	Eq. No. 2	2,4 units
Massecuite true purity	6 units	Eq. No. 3	0,7 units	Eq. No. 2	0,8 units

Measured experimental error : 1 unit of true purity in nutsch final molasses

These equations show that another reduction of about half a unit of true purity could be achieved in the next 10 hours, if extrapolation from 15 to 25 hours is assumed to be correct.

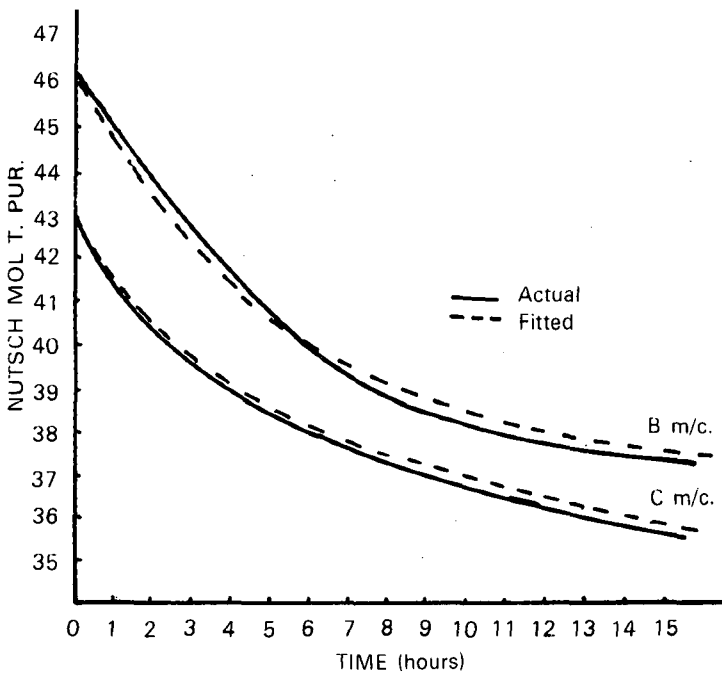


Figure 4: Actual and fitted values of Nutsch molasses true purity, against retention time.

3. Cooling rate -

The rates shown in Figure 3 were investigated in one of the three series. No significant effect could be found on final nutsch molasses purity.

The difference between the two rates investigated thus does not appear to affect the final exhaustion in the pilot mixer, after a retention of 15 hours. Effects on the rate of crystallisation however cannot be established, through this interpretation of the results.

4. Stirring rate -

Although stirring rate was investigated in two of the factorial series and in other shorter series, the results obtained are not very clear, mainly because of the difficulties in quantifying stirring.

Smythe⁵ shows that the effect of stirring rises relatively quickly to a plateau, after which large increases have very small further effects. If this is the case for low purity products, tests with stirring levels along that plateau would show stirring rate as having little effect on exhaustion. Although a wide range of stirring (1/4 to 2 rpm) was available it is quite possible that, due to the efficient design of the pilot crystalliser, rates are still too high, relative to factory equipment.

Broadly the results of the factorial series show that stirring rate does not affect the final nutsch molasses true purity, after retentions of 15 hours.

Again, this does not necessarily apply to crystallisation rate. In fact some indications that crystallisation rate does vary with stirring were obtained as discussed through curve fitting.

Curve fitting techniques

The use of curve fitting, as shown in Equation 4, raises some interesting possibilities.

From a theoretical approach, sucrose/water ratio in molasses is the dependent variable which must be used, as shown in Appendix 1. Then the equation

$$\text{Molasses} \frac{\text{suc}}{\text{H}_2\text{O}} = a + b \cdot e^{-ct} \quad \text{Equation (5)}$$

represents a simplistic model of batch crystallisation in which a is an indication of the ratio at infinite time, (a + b) is its initial value and c is related to rate of crystallisation.

The data obtained from the last factorial series may be used as an example. This series consisted of 19 runs, which include all the required combinations for high and low levels of massecuite total solids and true purity, stirring and cooling rates, plus a number of replicate runs. Samples were taken at regular intervals throughout the run and nutsch molasses extracted to investigate retention.

The results were averaged for the high and low levels of the various factors and sucrose/water ratios calculated. Curve fitting techniques were then used to yield the data shown in Table 4.

TABLE 4

Applying the model $\frac{\text{suc}}{\text{H}_2\text{O}} = a + b \cdot e^{-ct}$ to different levels of some factors.

Factor	Level	Constants			
		a	b	c	(a+b)
Massecuite NS ratio H ₂ O	Low (4,5)	2,32	1,06	-0,12	3,38
	High (5,8)	2,21	1,52	-0,12	3,73
Stirring	Low (1/4 r.p.m.)	2,11	1,39	-0,09	3,50
	High (2 r.p.m.)	2,38	1,19	-0,17	3,57

The following points may be made from the data in Table 4:-

- (i) Massecuite non-sucrose/water ratio does not affect the rate of crystallisation (i.e. value of constant c) but increases sucrose/water ratio in mother liquor at pan strike (i.e. value of constant b). The sucrose/water ratio in final nutsch molasses is however smaller for massecuites with a high non-sucrose/water ratio (value of constant a).
- (ii) The major difference between stirring levels is in the constant c that is in the rate, which changes by nearly 100%. The values of a are also different but this may be caused by heat generation with the higher stirring level. It was noticed that a nutsch molasses purity increase often occurred over the last few hours of retention time for those runs at high stirring, particularly with high total solids massecuites. This is due to the relatively high stirring efficiencies of the pilot-mixer and would not be present in industrial crystallisers.

Conclusion

This investigation has dealt entirely with the practical aspect of exhaustion, with the objective of obtaining answers concerning basic massecuite quality and crystalliser operation parameters.

In that context, massecuite non-sucrose/water ratio should be raised to the highest practical value, firstly by increasing total solids and secondly by dropping purity. Since the latter shows a relatively small effect on non-sucrose/water, large decreases are necessary for significant effects. This results in the need for maximum possible exhaustions in A's and B's as stressed by Jullienne⁶ and others.^{5,8} A word of caution might not be out of place here - equipment limitations must not be over-looked as, for example, increased centrifugation problems could well annul all the benefits due to high non-sucrose/water ratios.

Retention time was also shown to be highly significant. Although means of increasing retention are obviously not as direct as for massecuite total solids and purity it can be shown that important capacity increases result when C-massecuite purity is decreased, for the same cane throughput. A practical limit must exist but it is interesting to note that even with the

very efficient pilot-crystalliser and with other conditions as optimum as possible, exhaustion was still occurring at significant rates after 15 hours with massecuites at 40°C.

The curve fitting technique discussed provides a method for the quantification and comparison of stirring and cooling rates.

Although confirmation is needed, it would appear that increased stirring rate increases the crystallisation rate. Increases in stirring do not change the value of the exhaustion achievable under given conditions but promote the rate at which this maximum exhaustion is approached. There is a definite need for further work in that area. The effect of cooling rate was investigated rather briefly. Definite conclusions are not possible at this stage.

If the simple modelling approach can be applied to factory conditions, it would also allow quantification of effects such as massecuite quality under standard operations or of changes in process operations with more or less standard massecuite quality. Furthermore, comparison of the values of the constants between different mills or between a mill and the pilot mixer might help in pin-pointing problem areas.

Acknowledgments

This work would not have been possible without the co-operation and help of the various members of the project team. The author is particularly indebted to two of these members - Mr. C. van Lier (Darnall) who managed the project at the mill, and Mr. S. Baker (Operations Research) who dealt with all statistical aspects.

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Appendix 1

Derivation of a simplified model for crystallisation

1. Assumptions:

- a) No evaporation of water;
- b) First order rate equation;

c) Ratio $\frac{\text{mass sucrose}}{\text{mass water}}$ at saturation constant;

d) Rate constant k independent of time

(and hence temperature).

2. Differential rate law equation:

$$\frac{dC}{dt} = -k (C - C_s)$$

C = $\frac{\text{mass sucrose}}{\text{mass water}}$ in solution (molasses) at time t

$C_s = \frac{\text{mass sucrose}}{\text{mass water}}$ at saturation

$$\therefore \frac{dC}{(C - C_s)} = -k dt$$

3. Integrated rate law equation:

$$\ln (C - C_s) = -k.t + \text{constant}$$

At time zero: (i) t = t₀

(ii) C = C₀

where C₀ = initial $\frac{\text{mass sucrose}}{\text{mass water}}$

$$\therefore \text{constant} = \ln (C_0 - C_s)$$

$$\text{and } \ln (C - C_s) = -k.t + \ln (C_0 - C_s)$$

$$\therefore \frac{C - C_s}{C_0 - C_s} = e^{-kt}$$

$$\text{Thus } C = C_s + (C_0 - C_s) \cdot e^{-kt}$$

This is shown as Equation 5 i.e.

$$\text{Molasses } \frac{\text{suc}}{\text{H}_2\text{O}} = a + b \cdot e^{-ct}$$

where a = C_s

$$b = (C_0 - C_s)$$

$$\text{and } (a + b) = C_0$$

Appendix 2

Glossary of terms and abbreviations -

Ash

Sulphated ash

Nutsch

Mother liquor or molasses separated from a massecuite at any time prior to curing the massecuite in the factory centrifugals. The separation is done by pressure filtration.

Target purity

True purity ($\frac{\text{sucrose}}{\text{total solids}} \times 100$)
calculated from the formula:-
Molasses target purity

$$= 39,9 - 19,6 \log \frac{\text{reducing substance}}{\text{ash}}$$

as established by the Sugar Milling research Institute.

Target purity difference

True purity of molasses produced minus target purity

M/C

Massecuite

NS

Non-sucrose/water ratio

H₂O

Suc

Sucrose/water ratio

H₂O

T.P.

True purity